

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371**

17303-3

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

09/857680

INTERNATIONAL APPLICATION NO.

PCT/EP99/09659

INTERNATIONAL FILING DATE

December 7, 1999

PRIORITY DATE CLAIMED

December 10, 1998

TITLE OF INVENTION

LIME TREATMENT

APPLICANT(S) FOR DO/EO/US

Johannes Hendrikus Martinus de Pauw Gerlings

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

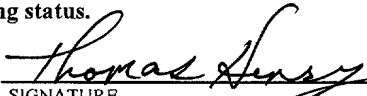
1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☒ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: Int. Prel. Exam Report

"Express Mail" label number EL68323610545. Date of Deposit June 9, 2001 I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR § 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Gail Mercer
Signature of Person Mailing Correspondence

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|---|------------------|--------------|-------------------|--|--|---|----|
| U.S. APPLICATION NO (if known, see 37 CFR 1.5) 09/857680 | | | | INTERNATIONAL APPLICATION NO EP99/09659 | | ATTORNEY'S DOCKET NUMBER 7303-3 | |
| 21. <input type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT = | | | | | | CALCULATIONS PTO USE ONLY | |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | | | \$ 860.00 | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | | | |
| Total claims | 15 - 20 = | 0 | x \$18.00 | | | | |
| Independent claims | 3 - 3 = | 0 | x \$80.00 | | | | |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | | + \$270.00 | | | | |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$ 860.00 | | | |
| <input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. | | | | + \$ 430.00 | | | |
| SUBTOTAL = | | | | \$ 430.00 | | | |
| Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | | | | |
| TOTAL NATIONAL FEE = | | | | \$ 430.00 | | | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property + | | | | | | | |
| TOTAL FEES ENCLOSED = | | | | \$ 430.00 | | | |
| | | | | | | Amount to be refunded: | \$ |
| | | | | | | charged: | \$ |
| a. <input checked="" type="checkbox"/> A check in the amount of \$ 430.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 23-3030 . A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038. | | | | | | | |
| NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status. | | | | | | | |
| SEND ALL CORRESPONDENCE TO: Thomas Q. Henry Woodard, Emhardt, Naughton, Moriarty & McNett 111 Monument Circle 3700 Bank One Tower Indianapolis, IN 46204 | | | | | | | |
| | | | | | |  SIGNATURE | |
| | | | | | | Thomas Q Henry NAME | |
| | | | | | | 28309 REGISTRATION NUMBER | |

09/857680

531 Rec'd PCT

07 JUN 2001

7303-3

IN THE UNITED STATES PATENT OFFICE

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|--|---|--------------------------------|
| In re patent application of: |) | Express Mail No. EL683236105US |
| |) | June 7, 2001 |
| Johannes Hendrikus Martinus de Pauw Gerlings |) | |
| |) | |
| Serial No. (unknown) |) | |
| |) | |
| Filed Herewith |) | |
| |) | |
| LIME TREATMENT |) | |
| (US National Stage of PCT/EP99/09659 |) | |
| filed December 7, 1999 |) | |

PRELIMINARY AMENDMENT

Hon. Assistant Commissioner of Patents

Washington, D.C. 20231

Sir:

Please enter the following preliminary amendment in the above-identified patent application:

IN THE CLAIMS

Please cancel claims 1 through 15.

Please add claims 16-30.

09/857680

CLAIMS – CLEAN COPY AS AMENDED

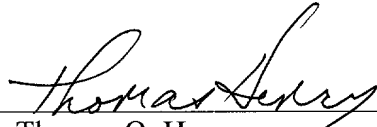
16. A method of obtaining a solution of calcium ions from lime, comprising
- (i) treating the lime with an aqueous solution of a polyhydroxy compound of the formula $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$ in which n is 1 to 6; and
 - (ii) optionally separating insoluble impurities from the solution resulting from (i).
17. A method according to claim 16, wherein the lime is carbide lime.
18. A method according to claim 17 wherein insoluble impurities are separated from the solution resulting from (i).
19. A method according to claim 16, wherein the lime is a product of the calcining of limestone or dolomite.
20. A method as claimed in claim 16, wherein the polyhydroxy compound is glycerol.
21. A method according to claim 16, wherein the sugar alcohol is sorbitol, mannitol, xylitol, threitol or erythritol.
22. A method according to claim 21 wherein the polyhydroxy compound is sorbitol.
23. A method as claimed in claim 16, wherein the polyhydroxy compound is employed as 10%-80% by weight solution in water.
24. A method as claimed in claim 21, wherein the polyhydroxy compound is employed as a 10% to 60% by weight solution.

25. A method as claimed in claim 20, wherein the glycerol is employed as a 60% to 80% by weight solution in water.
26. A method as claimed in claim 16, wherein the amount of lime is such as to provide 3-12 parts by weight per 10 to 80% by weight of the polyhydroxy compound.
27. A method as claimed in claim 16 effected at a temperature of 5°C-60°C.
28. A method of producing a calcium containing product comprising the steps of:
- (i) preparing a solution of calcium ions according to the procedure of any one of claims 1 to 12; and
 - (ii) adding to the solution from (i) a precipitating agent which causes precipitation of the desired calcium containing product.
29. A method as claimed in claim 28, wherein the precipitating agent is carbon dioxide and the product obtained is precipitated calcium carbonate.
30. A method of producing precipitated calcium carbonate from carbide lime comprising:
- (i) treating the carbide lime with an aqueous solution of sorbitol to extract calcium from the carbide lime;
 - (ii) separating the insoluble impurities from the solution resulting from (i); and
 - (iii) treating the solution with carbon dioxide.

REMARKS

Consideration and allowance of the above application is respectfully requested.

Respectfully submitted,

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PBA/NE/D088298PUS-TQH-130798

Version With Markings to Show Changes Made

09/857680

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CLAIMS

531 Rec'd PCT.

16
1.

A method of obtaining a solution of calcium ions from lime, comprising

(i) treating the lime with an aqueous solution of a polyhydroxy compound of the formula $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$ in which n is 1 to 6; and

(ii) optionally separating insoluble impurities from the solution resulting from (i).

17
2.A method according to claim ¹⁶1, wherein the lime is carbide lime.18
3.A method according to claim ¹⁷2 wherein insoluble impurities are separated from the solution resulting from (i).19
4.A method according to claim ¹⁶1, wherein the lime is a product of the calcining of limestone or dolomite.20
5.A method as claimed in any one of claims ¹⁶1 to 4, wherein the polyhydroxy compound is glycerol.21
6.A method according to any one of claims ¹⁶1 to 4, wherein the polyhydroxy compound is sorbitol, mannitol, xylitol, threitol or erythritol.22
7.A method according to claim ²¹6 wherein the polyhydroxy compound is sorbitol.23
8.A method as claimed in any one of claims ¹⁶1 to 7, wherein the polyhydroxy compound is employed as 10%-80% by weight solution in water.24
9.A method as claimed in claim ²¹6 or 7, wherein the polyhydroxy compound is employed as a 10% to 60% by weight solution.

16.

²⁵
~~10.~~ A method as claimed in claim ²⁰~~8~~, wherein the glycerol is employed as a 60% to 80% by weight solution in water,

²⁶
~~11.~~ A method as claimed in claim ¹⁶~~8~~, wherein the amount of lime is such as to provide 3-12 parts by weight per 100 parts by weight of the aqueous solution of the polyhydroxy compound.

²⁷
~~12.~~ A method as claimed in any one of claims ¹⁶~~1~~ to ~~11~~ effected at a temperature of 5°C-60°C.

²⁸
~~13.~~ A method of producing a calcium containing product comprising the steps of:

(a) preparing a solution of calcium ions according to the procedure of any one of claims 1 to 12; and

(b) adding to the solution from (a) a precipitating agent which causes precipitation of the desired calcium containing product.

²⁹
~~14.~~ A method as claimed in claim ²⁸~~13~~, wherein the precipitating agent is carbon dioxide and the product obtained is precipitated calcium carbonate.

³⁰
~~15.~~ A method of producing precipitated calcium carbonate from carbide lime comprising:

(a) treating the carbide lime with an aqueous solution of sorbitol to extract calcium from the carbide lime;

(b) separating the insoluble impurities from the solution resulting from (a); and

(c) treating the solution resulting from (b) with carbon dioxide.

Lime Treatment

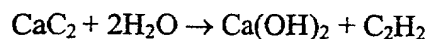
The present invention relates to a method of treating lime and more particularly, but not exclusively, to the treatment of lime containing insoluble impurities, to obtain a purified solution of calcium ions and also the use of said processing method to obtain useful, solid calcium containing products from the lime. The invention relates more particularly, but again not exclusively, to the treatment of carbide lime.

For the purposes of the present specification the term "lime" is used to describe both CaO and Ca(OH)₂ depending on the context.

Examples of prior art relevant to the present invention include US-A-3 340 003 which discloses the processing of dolomite by calcining and then dissolving the calcium oxide produced at high pH to obtain a solution of calcium succrate.

Also US-A-5 332 564 discloses the use of a calcium hydroxide water slurry with a very small amount of sucrose to produce rhombic precipitated calcium carbonate.

There is a need for a process which will enable a solution of calcium ions from lime particularly, but not necessarily, a lime containing insoluble impurities since the resulting calcium ion solution can be used for producing relatively valuable products. The need is particularly great in relation to carbide lime which is a by-product in the production of acetylene by the reaction of calcium carbide and water according to the equation



More particularly, carbide lime is comprised of calcium hydroxide and impurities resulting from the original calcium carbide and possibly also from the conditions under which the acetylene is produced.

The carbide lime is produced in amounts of approximately 3.5-4 times the weight of acetylene and is produced in dry powder form coming from a dry gas generator but mostly it is a water slurry from wet generators. Carbide lime is also known as carbide sludge, generator slurry, lime sludge, lime hydrate, and hydrated carbide lime.

Carbide lime is a grey-black substance. Typically it consists of around 90% by weight of calcium hydroxide (based upon the solids content of the carbide lime), the remainder being impurities which depend upon the method used to manufacture the acetylene and also upon the source of the materials used to manufacture the calcium carbide (normally made by roasting calcium oxide and coal). The main impurities are the oxides of silicon, iron, aluminium, magnesium, and manganese combined with carbon, ferrosilicon and calcium sulphate. Additionally if the carbide lime is stored outside, calcium carbonate, formed by the reaction of calcium hydroxide with carbon dioxide, may be present as an impurity.

Due to the impurities present in the carbide lime it has a low market value and is difficult to sell. The limited number of uses include use as a cheap base to neutralise acids or use in a slightly modified form as an agricultural fertiliser (Czechoslovakian Patent Application CS 8002961 – Jansky).

Since it does not have a significant commercial use, and also because the impurities which it contains renders disposal difficult, there are millions of tonnes of carbide lime stored in carbide lime pits all over the world. These pits are an ever increasing environmental problem.

Several methods as outlined below have been proposed to purify carbide lime but have various disadvantages:-

- a) Heating. The water and carbon impurities in the carbide lime can be removed by heating carbide lime in an oven at a temperature of at least

800°C to yield a "white" lime. However, this process is expensive to operate and has the disadvantage that oxide impurities are not removed.

- b) Simple filtration. The sludge may be subjected to a filtration operation. Unfortunately the particle size of the impurities contained within the carbide lime is similar to that of the particles of calcium hydroxide at 1 μm to 50 μm . Also as the impurities in the carbide lime tend to block filters with a thick sludge, the filters suffer from reduced efficacy and need constant replacement. Therefore simple filtration is ineffective.
- c) Dissolution of calcium hydroxide in water followed by filtration. As calcium hydroxide is sparingly soluble in water and as most of the impurities in carbide lime are insoluble, the calcium hydroxide can be extracted into an aqueous solution which is then filtered to remove the impurities. Unfortunately calcium hydroxide is only sparingly soluble in water; some 650 cubic metres of water are needed to dissolve one tonne of calcium hydroxide, therefore this method is impractical industrially.
- d) Solution of calcium hydroxide in water, using an ammonium salt as a solvating aid, followed by filtration. This method is identical to that described in (c) with the exception that anions, provided as chloride or the nitrate, are used to increase the solubility of the calcium hydroxide in water. This method is effective in reducing the amount of water needed to dissolve the calcium hydroxide but suffers from the drawback that the liquor containing the ammonium poses an effluent problem due to the relatively high ammonium salt concentrations, unless the ammonium solution is recycled after precipitation of the calcium with carbon dioxide.

Similar problem are also encountered in purifying other types of low quality (i.e. high impurity) lime.

The difficulties involved in purifying carbide lime and other low quality limes means that, in spite of the large available amounts of these materials, they are not used as a source of calcium for the production of higher value calcium products which have significant industrial applications. One example of such a product is Precipitated Calcium Carbonate (PCC) which is used as a functional filler in materials such as; paints, paper, coatings, plastics, sealants and toothpaste.

PCC is currently manufactured by the following methods: -

- a) Reacting an aqueous slurry of lime with carbon dioxide. This method suffers from the disadvantage that it is slow due to the low solubility of lime.
- b) Reacting a solution of lime with carbon dioxide. In this case problems arise initially as lime is only sparingly soluble in water (typical saturated concentration 2.16×10^{-2} molar at room temperature). The low concentration presents separation problems once the conversion to PCC is complete. Also due to the low lime concentration the reaction equilibria are such that, in the reaction with carbon dioxide, only about 30% of the lime is converted to PCC, the remainder being converted to $\text{Ca}(\text{HCO}_3)_2$, which remains in solution.

It is therefore an object of the present invention to obviate or mitigate the above mentioned disadvantages.

According to a first aspect of the present invention there is provided a method of obtaining a solution of calcium ions from lime, the method comprising

- (i) treating the lime with an aqueous solution of a polyhydroxy compound having three or more hydroxy groups and a straight chain of 3 to 8 carbon atoms; and

- (ii) optionally separating insoluble impurities from the solution resulting from (i)

We have found that the polyhydroxy compound solution as defined in the previous paragraph is an excellent solvent for the calcium and allows a much higher amount (e.g. about 65g/l) of the calcium ions present in the lime to go into solution than would be the case of use of only water. The method of the invention provides an efficient procedure for extracting calcium from lime. After removal of insoluble impurities, there remains a purified solution of calcium ions which may be used for the production of calcium containing products of considerably higher commercial value than carbide lime as discussed more fully below.

The lime used in the method of the invention may be any lime containing impurities that are insoluble in an aqueous solution of a polyhydroxy compound. A preferred example of such a lime is carbide lime, which contains carbon, ferrosilicon, calcium sulphate and the oxides of iron, silicon, aluminium, magnesium and manganese as insoluble impurities.

This aspect of the invention may however also be applied to the treatment of other types of lime (provided either as CaO or Ca(OH)_2 containing insoluble impurities to obtain a solution of calcium ions therefrom. Exemplary of such other limes are, low grade limes, the products obtained by calcination of limestone and that obtained by calcination of dolomite. In the latter case the method of the invention ensures separation of the MgO or Mg(OH)_2 since each is insoluble in the solution of the polyhydric alcohol. It is also possible for this aspect of the invention to be applied to the treatment of limes which contain no or relatively low amounts of impurities.

The polyhydroxy compound used in the method of the invention has a straight chain of 3 to 8 carbon atoms and should have significant solubility in water under the conditions employed.

Examples of polyhydroxy compounds which may be used are of the formula:



where n is 1 to 6. Thus for example the polyhydroxy compound may be glycerol (n=1). It is however more preferred that n is 2 to 6 and it is particularly preferred that the polyhydroxy compound is a sugar alcohol (a "hydrogenated monosaccharide"). Examples of sugar alcohols include sorbitol, mannitol, xylitol, threitol and erythritol.

Also useful as polydroxy compounds that may be employed in the invention are those having a straight chain of n carbon atoms where n is 4 to 8 and (n-1) of the carbon atoms have a hydroxyl group bonded thereto. The other carbon atom (i.e. the one without the hydroxyl group) may have a saccharide residue bonded thereto. Such compounds are hydrogenated disaccharide alcohols and examples include maltitol and lactitol.

Particularly preferred for use in the invention are the hydrogenated monosaccharide (e.g. sorbitol) and disaccharide alcohols because of their thermal stability which can be important for subsequent processing of the calcium ion solution (see below).

Mixtures of the above described polyhydric alcohols may also be used. Thus it is possible to use industrial sorbitol which, of the solids present, comprise about 80% sorbitol together with other polyhydroxy compounds such as mannitol and disaccharide alcohols. Examples of industrial sorbitol include Sorbidex NC 16205 from Cerestar and Meritol 160 from Amylum.

Depending on its solubility in water at the temperature used in the method, the polyhydroxy compound will generally be employed as a 10% to 80% by weight solution in water. When the polyhydroxy compound is a sugar alcohol, it will generally be used as 10% to 60% by weight solution, more preferably 15% to 40% by

weight solution in water. In contrast, glycerol will generally be used as 60% to 80% by weight solution in water, more preferably 65% to 75% by weight solution.

A second aspect of the invention relates to the treatment of carbide lime to obtain a solution of calcium ions therefrom. According to this aspect, the invention provides a method of obtaining a solution of calcium ions from carbide lime comprising:

- (i) treating the carbide lime with an aqueous solution of a polyhydroxy compound to extract calcium from the carbide lime, and
- (ii) separating insoluble impurities from the solution resulting from (i).

The polyhydroxy compound used in the second aspect of the invention may be as described for the first aspect of the invention. Additionally however this polyhydroxy compound may be a saccharide (e.g. a mono- or di-saccharide).

Examples of saccharides which are useful in the invention include glucose, fructose, ribose, xylose, arabinose, galactose, mannose, sucrose, lactose and maltose. Examples of saccharide derivatives which are useful in the invention include saccharide alcohols such as sorbitol and mannitol. It is particularly preferred that (for the second aspect of the invention) the polyhydroxy compound is chosen from the group consisting of sucrose, glucose, sorbitol and glycerol.

Depending on its solubility in water at the temperature used in the method of the second aspect, the polyhydroxy compound will generally be employed as a 10% to 80% by weight solution in water. When the polyhydroxy compound is a saccharide, or a derivative thereof, e.g. a sugar alcohol, it will generally be used as 10% to 60% by weight solution, more preferably 15% to 40% by weight solution in water. In contrast, glycerol will generally be used as 60% to 80% by weight solution in water more preferably 65% to 75% by weight solution.

The invention (both the first and second aspects) will be described fully with reference to the treatment of carbide lime but it is applicable *mutatis mutandis* to other forms of lime.

To produce a purified solution of calcium ions from carbide lime, it would generally be appropriate to extract an amount of carbide lime providing 3 to 12, more preferably 3 to 7 and ideally about 5 parts by weight calcium hydroxide with 100 parts by weight of the aqueous solution of the polyhydroxyl compound. Dry carbide lime from an acetylene generator may be extracted without further processing. However, in the case of wet carbide lime it will generally be preferred that this will be allowed to settle and subsequently dewatered prior to the extraction step. This can be best be done by filtration.

If the polyhydroxy compound used for extracting the calcium ions is susceptible to thermal decomposition then the extraction step may be effected at a temperature of 5°C to 60°C, although we do not preclude the use of temperatures outside this range. The admixture of the carbide lime and aqueous solution of the hydroxy compound should also be agitated to ensure maximum extraction of calcium ions into the aqueous liquor. Treatment times to obtain a desired degree of extraction will depend on factors such as the temperature at which the extraction is performed, degree of agitation, and concentration of the polyhydroxy compound but can readily be determined by a person skilled in the art.

Subsequent to the extraction step, the calcium ion solution is separated from insoluble impurities. Conveniently separation is effected by filtration, e.g. using a microfiltration unit, but other methods may be employed. If necessary a flocculating agent may also be used.

The resultant product is a purified calcium ion containing solution which may be used, for example, as a feedstock for producing industrially useful calcium containing, solid products. Such products are most conveniently produced by a precipitation reaction in which a chemical agent is added to the solution to precipitate the desired product. Thus, for example, by bubbling carbon dioxide through the

purified calcium ion containing solution it is possible to produce Precipitated Calcium Carbonate. Other precipitating agents which may be used include phosphoric acid, sulphuric acid, oxalic acid, hydrofluoric acid and citric acid.

Generally it will be appropriate to add the precipitating agent in at least stoichiometric amounts to the calcium contained in the solution. Alternatively or additionally, the supernatant liquor remaining after the precipitation reaction may be recycled for use in extracting calcium from a fresh batch of carbide lime. If the supernatant is to be recycled then it is desirable to dewater the carbide lime to prevent too much water entering the recycle stream and undesirably diluting this solution of the polyhydroxyl compound. Thus, as indicated previously, if the wet carbide lime is to be treated it should be allowed to settle and then dewatered. Alternatively or additionally, the supernatant may be heated to effect a degree of concentration thereof (by evaporation of water). If the supernatant is to be heated then it is highly desirable that the polyhydroxy compound is a sugar alcohol since these are resistant to heating and do not "brown" at the temperature required for such concentration. This ensures that the recycled, "concentrated" solution of the polyhydric alcohol is colourless and does not cause discolouration of the precipitated calcium carbonate. This is in contrast to, say, the use of sucrose as the extractant of the calcium ions where the concentrated, recycled sucrose solution may cause discolouration of the precipitated calcium carbonate although this may be tolerated for certain applications.

For the production of Precipitated Calcium Carbonate, carbon dioxide may be bubbled through the purified calcium ion solution using a conventional carbonation reactor. This reaction may be conducted at ambient temperature. Additives to coat the PCC, e.g. stearic acid derivatives, may be added at a later stage if required.

The PCC may be dewatered, washed and dried using equipment well known in the art.

The particle size of the PCC produced will depend upon parameters such as reaction time, temperature, CO₂ concentration and agitation speed.

The described method of producing PCC has the following advantages.

1. The method allows the production of high purity PCC.
2. The calcium ions, from which the calcium carbonate is generated are present in solution at a much higher concentration than would be the case of treating a suspension of lime.
3. Compared to the use of a suspension of lime for generating PCC, the method of the invention does not result in PCC being "deposited" on lime particles.
4. The method of the invention yields a PCC of narrow size distribution, small particle size and good colour.

The invention will be further illustrated by the following, non-limiting Examples

Example 1

To a 2 litre round bottomed flask fitted with a mechanical stirrer and thermometer was charged 250 grams of sorbitol in 660 grams of water at ambient temperature. To the resultant clear solution was charged 100 grams of crude carbide lime containing 50% moisture. The mixture was then stirred for a minimum of 20 minutes.

When the resulting solution containing the undissolved impurities was filtered the clear filtrate obtained was found to contain 4.1% w/w calcium hydroxide. The filtrate was charged to a carbonation reactor for precipitation of calcium carbonate by reaction with carbon dioxide gas, using the method described below.

To a 2 litre round bottomed flask fitted with a mechanical stirrer, pH probe and gas sparge tube was charged 4% calcium hydroxide in sorbitol solution (1000 grams). After sparging the mixture with carbon dioxide for approximately 10 minutes

the reaction to calcium carbonate was complete, indicated by the pH change from 11.8 to 7.0.

The precipitated calcium carbonate (PCC) was filtered and dried to yield 54.2 grams of calcium carbonate. The theoretical yield is 55.1 grams, implying a yield of 98.3%.

The fine, white PCC powder had the following properties.

| | PCC | Carbide Lime |
|--------------------|---------------------------|--------------|
| Mean Particle Size | ~2 μ m | 1-50 μ m |
| Crystal Structure | Calcite Rhombic Structure | - |
| Acid Insolubles | <0.2% | |
| Residual Fe | <0.05% | 0.12% |
| Residual Mg | <0.05% | 0.07% |
| Residual S | <0.1% | 0.35% |
| Residual Al | <0.05% | 1.15% |
| Residual Silica | <0.1% | 1.5% |

Example 2

To a 120 litre plastic drum was charged 43.2 kg water, 35.7 kg of a 70% w/w solids in water commercial grade of sorbitol (Sorbitol NC 16205) and 21.0 kg of a 22% w/w solids in water crude carbide lime suspension.

The mixture was stirred for 15 minutes. Then 1.5 litre of a flocculant stock solution was added to arrive at a final concentration of 25 ppm flocculant (Magnafloc LT25 from Ciba) on the total mixture.

The contents of the drum were stirred for 10 minutes and then the flocculants were allowed to settle for a period of 1 hour.

The resulting lime solution and settled impurities were filtered. The clear filtrate contained about 4.0% w/w of calcium hydroxide.

28 kg of the filtrate liquor was charged to a stainless steel carbonation reactor fitted with a turbine impeller, gas sparge ring, pH and temperature probe, feed liquor inlet and calcium carbonate product outlet.

The agitator was set at 600 rpm and the reactor contents were sparged with a gas mixture of 20% w/w carbon dioxide and 80% w/w nitrogen at a rate of 80g carbon dioxide per minute.

After approximately 20 minutes the carbonation reaction was completed, indicated by a pH change from 12.4 to about 7.0.

The formed precipitated calcium carbonate suspension was discharged from the reactor, filtered and washed in a pilot filter press.

The filter cake was dried to yield about 1.5 kg PCC, implying a yield of about 99%.

The calcite PCC powder had the following properties:

| | |
|--|---------------------|
| Mean particle size (Malvern Mastersizer) | 1.93 microns |
| Brightness (R457) | 97.3 |
| Tap density | 0.97 g/cc |
| HCl insolubles | 0.13% |
| pH value | 9.3 |
| BET surface area | 4 m ² /g |
| MgO | < 0.05% |
| Al ₂ O ₃ | 0.07% |
| SiO ₂ | 0.16% |
| Fe | 1 ppm |
| Mn | < 1 ppm |
| SO ₃ | 0.03% |

Example 3

57.5 grams of carbide lime, containing approximately 7.5 grams of impurities such as calcium carbonate, oxides and sulphates of silicon, iron, aluminium, magnesium, and manganese with carbon and ferrosilicon, were dissolved with stirring for 15 minutes in a solution containing 250 grams of sucrose in 750 grams of water.

The resulting solution containing undissolved black covered sludge-like impurities was filtered.

The clean solution containing about 50grams purified calcium hydroxide was transferred to a carbonation reactor for precipitation of calcium carbonate by reaction with carbon dioxide gas.

After 10-20 minutes of bubbling carbon dioxide the reaction to calcium carbonate was complete. The precipitated calcium carbonate (PCC) was filtered out of the suspension and dried, yielding 67 grams of calcium carbonate, (expected ~67.5 grams, implying a yield of over 99%).

The PCC powder had the following properties

| | |
|--------------------|---------------------------|
| Mean Particle Size | 3 μ m |
| Crystal Structure | Calcite Rhombic Structure |
| Acid Insolubles | <0.06% |
| Residual Fe | <3 ppm |
| Residual Mg | <3 ppm |
| Residual Mn | <3 ppm |
| Residual S | <3 ppm |
| Residual Al | 33 ppm |
| Residual Silica | 300 ppm |

CLAIMS

1. A method of obtaining a solution of calcium ions from lime, comprising
 - (i) treating the lime with an aqueous solution of a polyhydroxy compound of the formula $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$ in which n is 1 to 6; and
 - (ii) optionally separating insoluble impurities from the solution resulting from (i).
2. A method according to claim 1, wherein the lime is carbide lime.
3. A method according to claim 2 wherein insoluble impurities are separated from the solution resulting from (i).
4. A method according to claim 1, wherein the lime is a product of the calcining of limestone or dolomite.
5. A method as claimed in any one of claims 1 to 4, wherein the polyhydroxy compound is glycerol.
6. A method according to any one of claims 1 to 4, wherein the polyhydroxy compound is sorbitol, mannitol, xylitol, threitol or erythritol.
7. A method according to claim 6 wherein the polyhydroxy compound is sorbitol.
8. A method as claimed in any one of claims 1 to 7, wherein the polyhydroxy compound is employed as 10%-80% by weight solution in water.
9. A method as claimed in claim 6 or 7, wherein the polyhydroxy compound is employed as a 10% to 60% by weight solution.

10. A method as claimed in claim 5, wherein the glycerol is employed as a 60% to 80% by weight solution in water.
11. A method as claimed in claim 8, wherein the amount of lime is such as to provide 3-12 parts by weight per 100 parts by weight of the aqueous solution of the polyhydroxy compound.
12. A method as claimed in any one of claims 1 to 11 effected at a temperature of 5°C-60°C.
13. A method of producing a calcium containing product comprising the steps of:
- (a) preparing a solution of calcium ions according to the procedure of any one of claims 1 to 12; and
 - (b) adding to the solution from (a) a precipitating agent which causes precipitation of the desired calcium containing product.
14. A method as claimed in claim 13, wherein the precipitating agent is carbon dioxide and the product obtained is precipitated calcium carbonate.
15. A method of producing precipitated calcium carbonate from carbide lime comprising:
- (a) treating the carbide lime with an aqueous solution of sorbitol to extract calcium from the carbide lime;
 - (b) separating the insoluble impurities from the solution resulting from (a); and
 - (c) treating the solution resulting from (b) with carbon dioxide.

DECLARATIONRegistered Practitioner Information
(Supplemental Sheet)

| Name | Registration Number | Name | Registration Number |
|-------------------------|---------------------|------|---------------------|
| Harold R. Woodard | <u>16,214</u> | | |
| C. David Emhardt | <u>18,483</u> | | |
| Joseph A. Naughton, Jr. | <u>19,814</u> | | |
| John V. Moriarty | <u>26,207</u> | | |
| John C. McNett | <u>25,533</u> | | |
| Thomas Q. Henry | <u>28,309</u> | | |
| James M. Durlacher | <u>28,840</u> | | |
| Charles R. Reeves | <u>28,750</u> | | |
| Vincent O. Wagner | <u>29,596</u> | | |
| Steve Zlatos | <u>30,123</u> | | |
| Spiro Bereveskos | <u>30,821</u> | | |
| William F. Bahret | <u>31,087</u> | | |
| Clifford W. Browning | <u>32,201</u> | | |
| R. Randall Frisk | <u>32,221</u> | | |
| Daniel J. Lueders | <u>32,581</u> | | |
| Kenneth A. Gandy | <u>33,386</u> | | |
| Timothy N. Thomas | <u>35,714</u> | | |
| Kerry P. Sisselman | <u>37,237</u> | | |
| Kurt N. Jones | <u>37,996</u> | | |
| John H. Allie | <u>39,088</u> | | |
| Holiday W. Banta | <u>40,311</u> | | |
| Troy J. Cole | <u>35,102</u> | | |
| L. Scott Paynter | <u>39,797</u> | | |
| J. Andrew Lowes | <u>40,706</u> | | |
| Charles J. Meyer | <u>41,996</u> | | |
| Matthew R. Schantz | <u>40,800</u> | | |
| Gregory B. Coy | <u>40,967</u> | | |
| Lisa A. Hiday | <u>40,036</u> | | |
| John V. Daniluck | <u>40,581</u> | | |
| Christopher A. Brown | <u>41,642</u> | | |
| C. John Brannon | <u>44,557</u> | | |
| Jason J. Schwartz | <u>43,910</u> | | |
| Arthur J. Usher IV | <u>41,359</u> | | |
| Douglas A. Collier | <u>43,556</u> | | |
| Brad A. Schepers | <u>45,431</u> | | |
| Scott J. Stevens | <u>29,446</u> | | |
| James B. Myers | <u>42,021</u> | | |
| John M. Bradshaw | <u>46,573</u> | | |
| C. Amy Ng Smith | <u>42,931</u> | | |
| Charles P. Schmal | <u>45,082</u> | | |
| Edward E. Sowers | <u>36,015</u> | | |

6/6/01

DECLARATION AND POWER OF ATTORNEY FOR PATENT APPLICATION

Attorney Docket Number

7303-3

First Named Inventor

Johannes Hendrikus Martinus de Pauw Gerlings

SEP 10 2001

PATENT & TRADEMARK OFFICE

☐ Declaration submitted with Initial Filing

☒ Declaration Submitted after Initial Filing (surcharge (37 CFR 1.16(e)) required)

COMPLETE IF KNOWN

Application No.

09/857,680

Filing Date

Group Art Unit

Examiner's Name

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

LIME TREATMENT

the specification of which (check one)

☐ is attached hereto.

☒ Was filed on December 7, 1999 as United States Application No. or

PCT International Application No. PCT/EP99/09659

☐ And was amended on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YY) | Priority Not Claimed | Certified Copy Attached? | |
|-------------------------------------|---------|--------------------------------|----------------------|--------------------------|-------------------------------------|
| PCT/EP99/089659 | PCT | 12/07/99 | | Yes | No |
| 9827033.3 | GB | 12/10/98 | | <input type="checkbox"/> | <input checked="" type="checkbox"/> |

I hereby claim the benefit under 35 U.S.C. 119(e) of any United States provisional application(s) listed below.

| Application Number(s) | Filing Date (MM/DD/YYYY) | <input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority data sheet PTO/SB/02B attached hereto. |
|-----------------------|--------------------------|--|
| | | |
| | | |
| | | |

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

| U.S. Parent Application or PCT Parent Number | Parent Filing Date (MM/DD/YYYY) | Parent Patent Number (if applicable) |
|--|---------------------------------|--------------------------------------|
| | | |

Additional US or PCT International application numbers are listed on a supplement priority data sheet PTO/SB/02B attached hereto.

As a named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

☐

☒

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OR

Registered practitioner(s) name/registration number listed below.

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| Name | Registration Number | Name | Registration Number |
|-----------------|---------------------|------|---------------------|
| Thomas Q. Henry | 28,309 | | |

☒ Additional registered practitioner(s) named on supplemental Registered Practitioner Information sheet PTO/SB/02C attached hereto.

Direct all correspondence to :

☐

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OR


☒

Correspondence address below

| | | | | | |
|-----------|--|-----------|---------------|-----|--------------|
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Full name of sole or first inventor:

| | | | |
|---------------------------------------|---|------------------------|------------------|
| Given Name (first and middle, if any) | Johannes Hendrikus Martinus | Family Name or Surname | de Pauw Gerlings |
| Inventor's Signature: |  | Date of Signature: | 24 August 2001 |
| Residence: (City, State, Country) | St. Genis-Pouilly, France | | |
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